Final Report - Phase I

Small Business Innovation Research Program

U. S. Navy Contract No. N00014-93-C-0193

Issued by the Office of Naval Research

Project Title:

Process Modeling of a Novel Plasma Assisted Alloy Plating

Principal Investigator:

Mandar Sunthankar

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Project Summary:

Plasma Assisted zinc-cadmium alloy plating will reduce the use of cadmium and minimize hazardous waste in many plating operations. The purpose of the proposed research is to understand this dry plating process for its commercial application. In this process, the composition of the zinc-cadmium alloy needs to be varied in situ as desired. Consequently, the primary objective of the Phase I effort is to study the effect of process parameters on the alloy composition. The secondary objective is to measure the lubricity of the alloy as a function of its composition.

Both the primary and secondary objectives have been accomplished successfully. The fractional factorial design of experiments has been used to model the cumulative effect of dry plating process parameters on the zinc-cadmium alloy composition. Steel substrates were used for alloy plating. The chemical composition was determined using Energy Dispersive Spectrometric (EDS) x-ray analysis. The lubricity was measured in terms of coefficient of friction using the pin-on-disk method. The process model developed predicts that the alloy composition is directly proportional to the zinc source temperature. The feasibility of plating a wide range of compositions, from 8% zinc in zinc-cadmium to 100% zinc, has been demonstrated. In addition, data indicates that the lubricity of a range of dry plated zinc-cadmium alloys is superior to that of zinc. In conclusion, the dry zinc-cadmium alloy plating process has a promising commercial potential.

<u>Commercial Potential</u>: The dry plating process offers an economical alternative to conventional zinc and cadmium electroplating because it eliminates liquids and recycles solid metals in situ. This process has substantial commercial potential in plating fasteners, connectors, high strength steel components, steel rolls and construction wires used in the U.S. Navy as well as aerospace, steel and automobile industries.

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Final Report, U.S. Navy Contract# N00014-93-C-0193

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1. Introduction

Electroplated cadmium is preferred in many large-scale applications because of its superior lubricity as well as corrosion resistance in marine environment compared to that of other coatings[1]. In cadmium electroplating operations, exposure to cadmium dust is a safety issue and disposal of cadmium sludge and effluents are an environmental issue[2]. Consequently, there is substantial interest in reducing the use of cadmium and related waste. However, two decades of extensive effort in this area has yet to result in an effective economical solution.

Dry plating is a new and unique process developed at the IonEdge Corporation with promising pollution prevention potential. Dry plating eliminates use of liquid chemicals and prevents solid waste using in situ reclaim. In recent years, zinc-cadmium alloys have been qualified by the automobile industry for some fastener applications[3]. Also, it has been reported that certain zinc-cadmium compositions exhibit corrosion resistance superior to cadmium in most environments[3,4]. Environmentally safer zinc plating alone does not exhibit the frictional property required to replace cadmium. The frictional coefficient of zinc is relatively higher than that of cadmium. The addition of cadmium is likely to enhance the lubricity of zinc and bring it into an acceptable range for fasteners. The proposed effort is intended towards using a non-liquid chemical process for plating a range of zinc-cadmium alloys and studying the frictional property with respect to their composition.

1.1 Research Objectives:

The corrosion properties of certain zinc-cadmium alloys are known to be superior to electroplated cadmium. In addition, the automobile industry has qualified the zinc-cadmium alloy plating for fasteners. These alloys would reduce cadmium waste. This waste reduction could be further improved using the dry plating process.

The investigations in this research are designed to improve the understanding of the dry plating process and its effect on the alloy composition. This methodology has resulted in the following objectives:

(i) Using the fractional factorial design of experiments, develop a model for the alloy composition as a function of independent process variables (e.g., anode voltage, source temperature); and

(ii) Correlate the lubricity in terms of coefficient of friction of the dry plated alloy with its composition.

These studies are important for the application of the dry plating technology in the commercial sector.

2. Background

There is substantial interest in reducing cadmium waste in electroplating. An estimated 1,166 cadmium plating facilities across the U.S. discharge large quantities of toxic effluents into waste-water[2]. A byproduct of this process is toxic sludge which has to be disposed of at government regulated land sites. In order to comply with various regulations, pollution control hardware which costs over $650,000 is required[5]. In addition, the reported cost of waste-water treatment and sludge disposal is approximately $1,200 per day in a typical facility[6]. With decreasing number of land sites and stricter discharge limits, the cost of the sludge disposal is escalating rapidly[7].

A number of alternative material coatings such as zinc, zinc-iron, zinc-nickel, aluminum, polymers and composites are replacing cadmium in some applications in which properties and/or cost can be compromised[8]. However, in many naval and aerospace applications, fasteners and electrical connectors in which critical dimensions or properties cannot be compromised, suitable economical alternatives are not available[9]. In these applications, the dry plating is a promising alternative.

A new coating recently qualified by the Ford Motor Company is a 50/50 zinc-cadmium alloy[3], i.e., 50% by weight zinc in cadmium (Ford Specification S-54M). This alloy contains 50% less cadmium in deposited coatings. The 50/50 zinc-cadmium (Zn-Cd) alloy shows suitable combination of properties of both zinc and cadmium, and is superior to cadmium in corrosion properties[3]. The outdoor exposure studies of competing coatings for five years indicated that 75/25 zinc-cadmium alloys outperform other coatings in every environment tested, including marine environment[4]. The lubricity properties of zinc-cadmium alloys were not reported, however.

Various compositions of the zinc-cadmium alloy coatings are currently applied using the mechanical barrel plating process[3,4]. This is a liquid chemical operation free of cyanide and chelates[7]. However, significantly larger amounts of cadmium

and other toxic chemicals are discharged following each batch of plating compared to electroplating. This results in a cost intensive operation[10].

Therefore, a plating method which could minimize discharge and disposal of toxic chemicals is desirable. The dry plating has addressed this need with three unique features: (a) the dry plating process eliminates liquid chemicals; (b) its plating rate is competitive with electroplating; and (c) solid waste is minimized using in situ reclaim and recycle. Furthermore, the zinc-cadmium alloys will reduce the amount of cadmium byproducts released in the environment by discarded components.

2.1 The Dry Plating Concept:

Zinc and cadmium exhibit relatively higher vapor pressure compared to most other metals. These metals also vaporize (sublime) at temperatures well below their melting points. The dry plating is performed in a glow discharge apparatus in which a large area sublimating source, a foil or sheet, is part of the cathode arrangement as shown in the schematic of Fig.1.

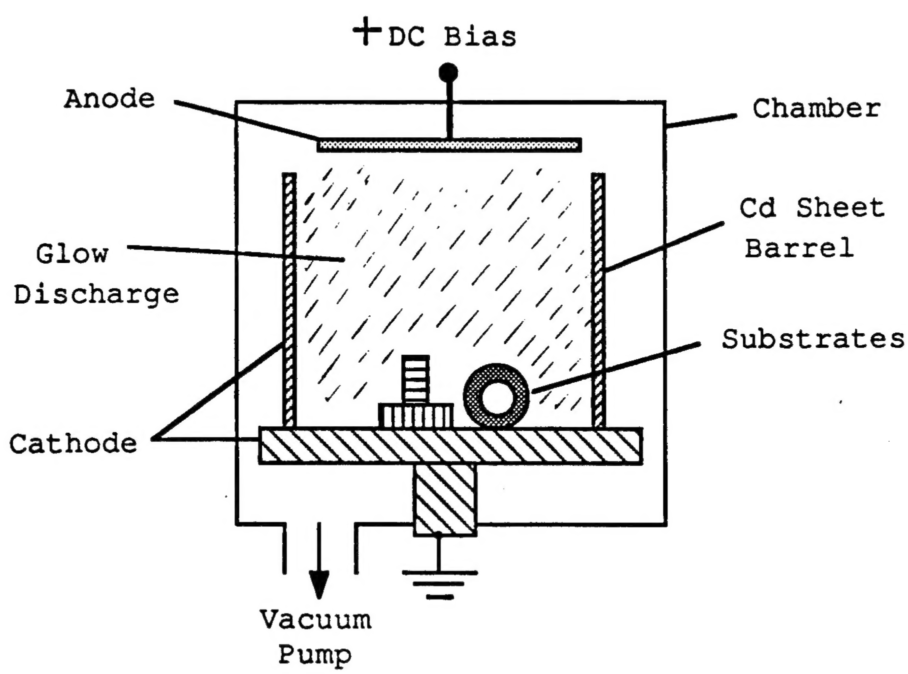


Fig. 1: A schematic of the dry plating concept.

The parts to be coated are placed on the support cathode base. The large area source is bombarded with a portion of the same energetic ions and neutrals which impinge on the cathode base. This energy transfer results in source heating and sublimation at high rates. Alternatively, external thermal heating of the source foil accomplishes the same result. In the reclaim/recycle concept of dry plating, the same sublimation property is utilized for prevention and recycling of extraneous metal deposits from chamber walls using such an energy transfer method. The feasibility of this reclaim concept has been tested and verified. A photograph of the equipment used in proving these concepts in its early stages is shown in Fig.2.

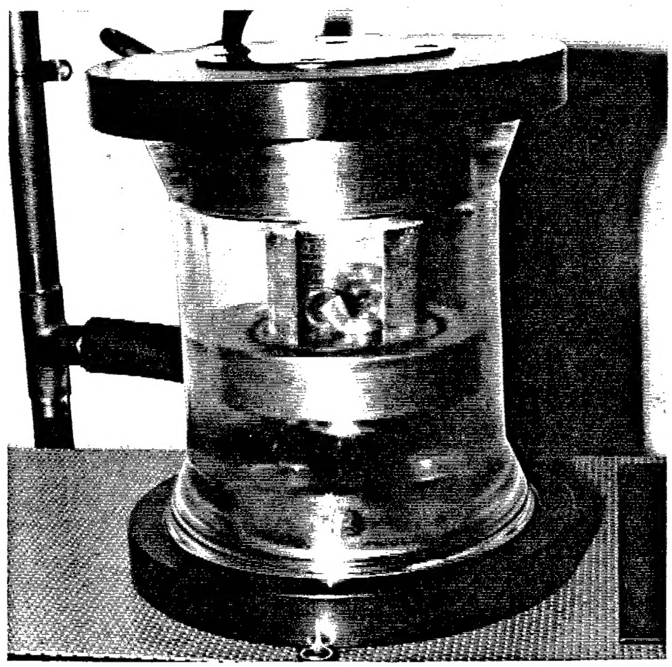


Fig.2: Apparatus used in the early feasibility studies.

The scattered, non-directional nature of the glow discharge (plasma) enhanced process produces excellent plating uniformity without rotation of the parts. In dry plating, surface cleaning before plating is performed in the same process cycle using neutral gas ion bombardment. There are no by-products or waste generated in this "dry" cleaning.

Plating rates competitive with electroplating have been accomplished in this process. The photograph of Fig.3 shows dry

plated fasteners of complex shapes. The typical, loading to unloading cycle time for a 0.5 mil thick plating is less than 10 minutes. The plating rates of up to 17μm/min have been demonstrated for zinc and cadmium.

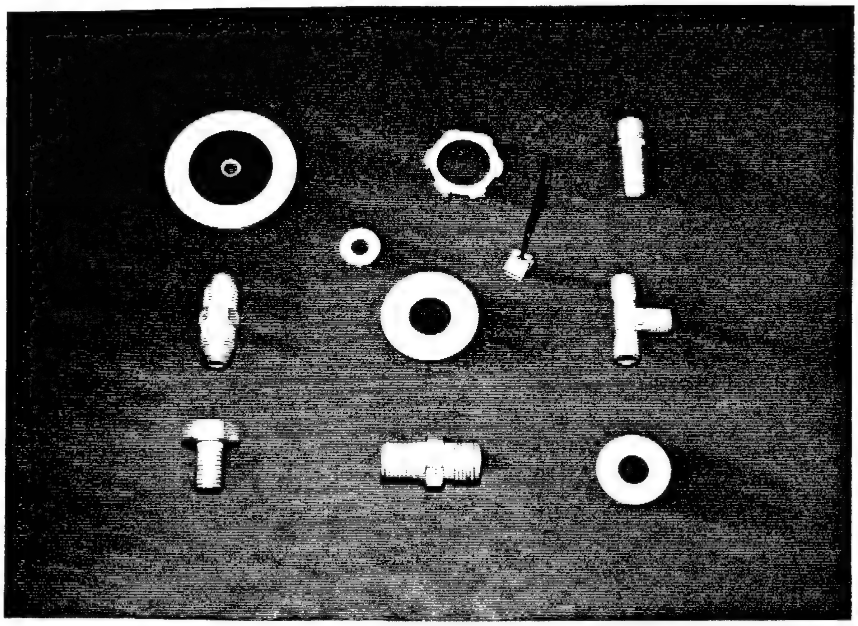


Fig.3: Dry plated fasteners of various shapes

3. Proposed Phase I Research Plan

In the dry plating of zinc-cadmium alloy, simultaneous plating of zinc and cadmium vapor species is conducted under glow discharge conditions. The glow discharge offers following advantages: a) the collision of ionized neutral gas molecules with zinc and cadmium particles results in atomic mixing of the species before plating; b) the bombardment of the ionized species on the substrate enhances adhesion of the growing layer to the substrate; and c) energetic particle bombardment on the surface densifies the alloy layer.

3.1 Statistical Design of Experiments - SDE:

A brief description of this method is explained below. Exhaustive details of the SDE could be found elsewhere[11,12]. The objective of statistical design of experiments is to maximize the information obtained in an experiment with minimum number of trials. These experiments define the relationship between independent variables (factors) and dependent variables (response). The proposed effort is designed to use two-factor (voltage, source temperature) experiment to observe the effect on response (wt% Composition). In this design, two settings (levels) of each factor will be used: Low (-) and high (+). The number of trials then would be $l^p=4$ where l= number of levels and p is the number of factors.

In one-at-a-time common approach, changing one factor while holding others constant leads to incomplete coverage of the experimental space, missing relationship between the factors and possibility of false assumptions. As the number of factors increase, one-at-a-time strategies are even more prone to error. Examination of the Table I-a indicates that the low-low (- -) combination is absent leaving that portion of the experimental space unexamined. One of the advantages of factorial experiment is that every trial run can be used to obtain information about every factor in the experiment. Also, factorial experiments provide higher precision in estimating the effects.

Table I

	I - a			I - b		
	<u>One-at-a-time</u>			<u>Complete Factorial</u>		
	Factor	Level	Response	Factor	Level	Response
Trial #	A	B	(Composition)	A	B	(Composition)
1	+	+	z_1	-	-	Z_1
2	-	+	z_2	+	-	Z_2
3	+	+	z_1	-	+	Z_3
4	+	-	z_3	+	+	Z_4

Table II: Computational Analysis

Trial	Mean	x_1	x_2	x_1x_2	Z(μm/ min.)
1	+	-	-	+	10
2	+	+	-	-	15
3	+	-	+	-	12
4	+	+	+	+	17
Sum +:	54	32	29	27	
Sum -:	0	22	25	27	
Overall Sum:	54	54	54	54	
Difference:	54	10	4	0	
Factor Effect:	13.5	5	2	0	

<u>Computational Analysis:</u> The computing table for analysis of 2^2 factorial design is shown in Table II above. For illustration, typical numbers based on past experience were entered for dep. rates (μm/min.). Here, Z = average response to the corresponding trial; Sum+ and Sum- are summation of responses corresponding to the sign in the factor columns; Difference is the difference in Sum+ and Sum- in the column. Overall Sum should be the same in all columns. Finally, Factor Effect is the Difference divided by the number of + signs in that column.

<u>Significance of Factor Effect:</u> If the computed factor effect is larger (in absolute value) than the "Minimum Significant Factor Effect" (MSF), it can be derived from an appropriate t-test of significance as follows:

$$MSF = t\ s\ \sqrt{(2/mk)}$$

where t = value of student's "t" at desired probability,

m = number of plus signs in the column,

k = number of replicates of each trial,

s = pooled std. dev. of a single response observation

The factor effect value reveals which factors exert strong influence on the response, and helps interpret the results.

The Two-Level Factorial Model: The model for coded factors x_j is $Z = a_0 + a_1x_1 + a_2x_2 + a_{12}x_1x_2 + \ldots\ldots$ (higher order terms) where Y = predicted response.

The coefficients in this model are half of the corresponding factor effects, since the coded levels (+1) and (-1) differ by two units. For the example above, the equation would be

$$Z = 6.75 + 2.5x_1 + 1x_2 + 0x_1x_2$$

With a slight modification of this design, center points can be added between the (+) and (-) levels. This allows prediction of any significant curvature in the response using "minimum significant curvature" formula as in the case of MSF.

3.2 Zinc-Cadmium Alloy Plating:

In the zinc-cadmium alloy plating feasibility study, sections of zinc and cadmium foil were placed on the cathode across from each other as shown in the photograph of Fig.4.

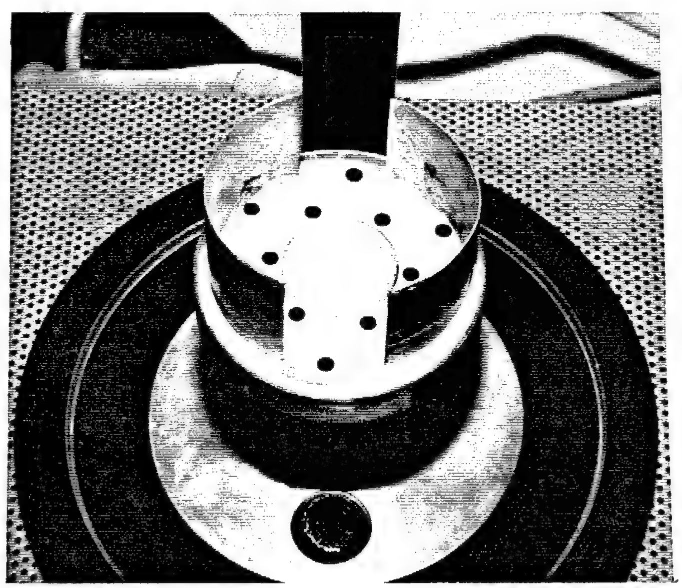


Fig.4: The source cathode configuration for alloy plating.

In an adequately energized plasma, the collision of ionized argon molecules with zinc and cadmium foils resulted in simultaneous vaporization of both species and alloy plating on substrates. In the presence of ion bombardment, each foil reached an equilibrium temperature, and sublimed at the rate proportional to its vapor pressure at that temperature. Consequently, the ratio of the area of respective foils was adjusted to accomplish the desired composition on the substrate. Only one composition was feasible for each area ratio. This limits the flexibility in adjusting the composition as desired in manufacturing situations. However, <u>if the vapor pressure is varied by varying the foil temperature using thermal heating, composition could be varied or adjusted as desired on the shop floor</u>. The dry plating lab apparatus of Fig.2 was later modified as shown in the schematic of Fig.5 for use in this research.

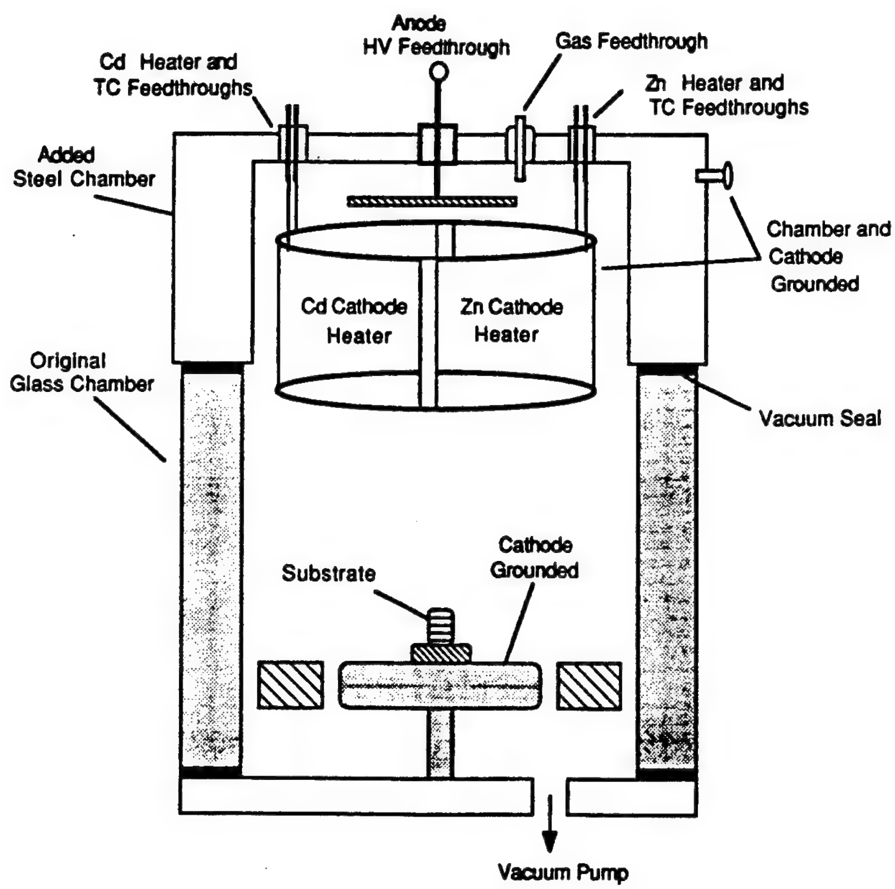


Fig.5: A schematic of the proposed zinc-cadmium alloy plating set up.

Task I: <u>The Composition Study</u>:

In the preliminary studies conducted, anode bias voltage and source foil temperature were identified as two significant factors which influence the alloy composition. The alloy composition is the continuous response (note that this composition will be measured as the wt% zinc in the zinc-cadmium alloy). In this research, the dry plating process model for the composition will be derived. For increasing the confidence level in the sample results, two substrates will be deposited in each trial and two replicates of each trial will be conducted. The experimental sequence for each trial is outlined below.

The following factorial will be studied:

Factor x1 = voltage → Levels = 700V (-), 1100 V (+).

Factor x2 = Zn temp → Levels = 150 °C (-), 350 °C (+).

Constants: Ar pressure = 40 mT, Cadmium Temp. = 100°C

Experimental Sequence: Zn-Cd Alloy Composition

a. Substrate Material:	Commercial grade, cold-rolled mild steel, 2 mm thick
Substrate Size:	Cut into 1.5 x 1.5 cm samples.
Number of substrates:	2 each trial
b. Substrate Preparation:	Polish to 10 µm ± 20% finish with Buehler alumina slurry. Ultrasonically degrease with acetone and alcohol, and dry.
c. Zn-Cd Plating:*	Ion clean steel substrate, 2 minutes, 100 mT Ar, 500 V. Deposit Zn-Cd alloy using selected factorial, one at a time. Ar pressure constant at 40 mT, Cd temp. const. = 100°C.
d. Composition Measure:	Energy Dispersive Spectrometric (EDS) x-ray analysis to determine composition by %wt on each substrate. Averaged on 2 substrates by EDS (wt% Zn in Zn-Cd).
e. Test Location:	All the steps above will be performed in the Materials Laboratory of the Colorado State University (CSU).

The trials will be replicated. the total number of experiments will be twelve. An equation will be derived representing the process relationship with composition.

Task II: The Lubricity Study :

The lubricity will be measured in terms of coefficient of friction. The frictional coefficient correlates well with the torque requirements in fastener installations. For example, aluminum has higher coefficient than cadmium. Consequently, a higher torque is required to install aluminum coated fasteners[13]. The objective of this study is to correlate the frictional coefficient of the alloy with its composition. The lubricity is likely to improve with increasing cadmium content. Four zinc-cadmium alloys of increasing zinc content will be dry plated on mild steel washers. The frictional coefficient will be measured using standard pin-on-disk method. The apparatus consists of a rotating, dry plated steel washer or disk and a stationary hemispherical mild steel pin. This combination would simulate practical conditions in the field. The coefficient of friction will be plotted against composition to observe the trend.

4. Details of the Phase I Research Performed

4.1 The Statistical Design of Experiments (SDE):

The Factorial Design: Factorial designs permit estimation of the effect of several factors simultaneously. The two level factorial designs are highly useful for a wide variety of problems. These are easy to plan and analyze, and provide adequate models for responses which do not have strong curvatures in the experimental region. The two level factorial can determine the main effect of each factor plus the interaction of the factors in combination. As a good design strategy, the high (+) and low (-) levels should be as far apart as possible within the limitations of the apparatus. These limitations were defined early in the experiments.

The Experimental Error: The other important consideration is the experimental error, either random or bias, which has to be minimized. The bias errors have been minimized using the randomized trial order provided by a calculator. The random error was minimized by reducing the variations in values set for the bias voltage, source temperatures as well as the pressure. The system was tested for repeatability of the these process conditions. For example, the argon pressure was held within 2 millitorr of the trial setting during experiments. For the small sample size used in each experiment (less than 3), the "t-static" provided a convenient and sound method for determining if the sample data is representative of a trial under evaluation

The Response Curvature: The factorial design as proposed does not provide an estimate of the curvature of the response in the experimental region. It is always desirable to check a "lack of fit" of the derived model. Consequently, the proposed method has been modified to estimate this curvature using a statistical technique. A relatively simple and time saving exercise is to run points at the middle (0,0) value of all factors. These center points can be used only for continuous

factors as in the case of source temperature, bias voltage or pressure used. The degree of curvature is estimated using the difference in average response values of design points and center points. If the curvature is severe, this method does not provide an accurate prediction of the nonlinearity. However, it will point out if there is a need of running a full response surface design. In that case, twice as many number of trials may be required.

Significance of Curvature Effect: The appropriate t-test of significance for the "Minimum Significant Curvature " effect (MSC) is

$$MSC = t\ s\ (1/mk + 1/c)$$

where t, s, m, k are as noted earlier

c = the number of center points

The above formula for MSC indicates that it is desirable to replicate the center point more heavily than any other design point.

4.2. The Apparatus:

In this research, a new dry plating apparatus specifically developed and assembled in-house for advanced process studies was used (see Fig.6). This horizontal plating system was selected over the proposed small verticle unit shown in Fig.5 because of larger size and better control over most process parameters. In addition, the new system is more representative of the apparatus to be developed for commercial application. A schematic of this dry plating process chamber of is shown in Fig.7. This stainless steel chamber is 61cm dia x 76cm long (24" dia x 30"). The additional feature of the apparatus is a proprietary in situ reclaim test chamber within the main chamber. Up to 25cm (10") diameter large single objects of most shapes, including racks for loading small parts, can be accommodated easily for plating in this system. The infrared (IR) source heaters (1kW, Infrasource, UK) are 24cm x 5cm x 6mm thick (9.4"x2"x0.25") and independently heated to the desired temperature.

Fig.6: Advanced dry plating chamber and control systems.

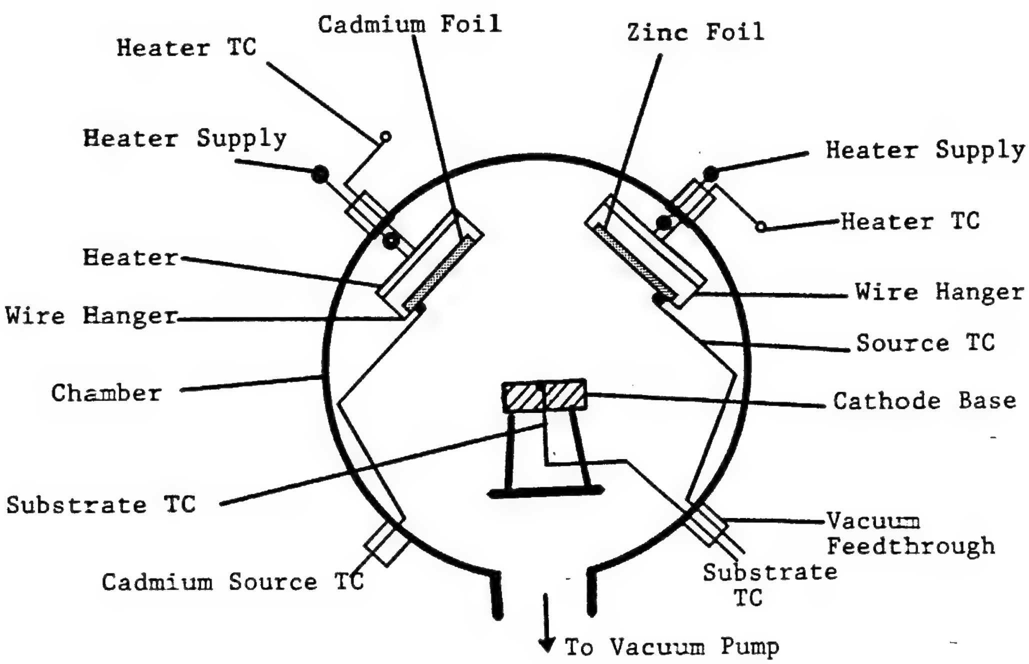


Fig.7: A schematic of the dry plating chamber shown in Fig.6.

The source foil plates are suspended below the heater at a distance of 1.5cm using wire hangers. The chamber argon pressure is controlled using MKS pressure controller to within

$\pm 1x10^{-6}$ Torr at heater temperatures up to 500°C. The base pressure obtained using diffusion pump remained consistently below $2x10^{-6}$ Torr. An anode located in close proximity to the electrically grounded zinc source foil provided for initiating glow discharge (plasma). The plasma was controlled using ORAM high voltage DC power supply. The plasma has been operated to 2kV at 1A anode current and at pressures as low as $5x10^{-4}$ Torr. The plasma was used to enhance vaporization and improve plating adhesion. The heater temperatures were ramped as desired and controlled using Eurotherm controllers in a feedback loop with heater thermocouples. The substrate temperature and individual source temperatures were monitored independently using separate digital thermometers. Later, zinc and cadmium sources were heated independently and vaporized simultaneously. Considerable time spent in this preparation resulted in acceptable and repeatable performance of the apparatus.

4.3 Dual Source Vaporization:

The data available from the literature[14] indicated the range of source temperatures below melting point at which source could be vaporized in plasma at reasonable plating rates of 0.1 to 5μm/min. This range is highlighted in the Table III below.

Table III[14]

	Vapor Pressure (Torr)				
	10^{-1}	**10^{-2}**	**10^{-3}**	10^{-4}	10^{-5}
Cd, temp °C :	320	**265**	**217**	177	146
Zn, temp °C :	408	**344**	**292**	247	209

These were considered as first approximation of the high (+) and low (-) factor levels for the source temperature. During preliminary vaporization tests, small variations in heater temperature resulted in large variations in source foil temperature. Based on the heat capacity of zinc (0.093 W/cm/°K) and cadmium (0.056 W/cm/°K), aluminum heat absorbing plates (Cp = 0.26 W/cm/°K) of thickness 1.5mm and 3.0mm respectively were

attached to source foils using metal clips. This arrangement worked acceptably. Rapid heater temperature ramp-up then became possible and the rate was set to 30 °C per minute. At this rate, process cycle time was typically less than 25 minutes. This limitation is less likely in manufacturing where thick source plates or bars could be used and maintained at high temperatures.

4.4 Experimental Set Up:

Source foils used for both zinc and cadmium were 99.5% pure (Goodfellow, UK) and 15cm x 3.8cm x 0.5mm thick (6" x 1.5" x 0.02"). After attaching the temperature stabilizing aluminum backing plates described earlier, these were suspended at a distance of 1.5cm and parallel to the ceramic IR heaters using 24 gauge steel wire hangers. The source foils acted as cathode when electrically grounded with the help of wire hangers. The heaters were embedded with thermocouples for close-loop temperature control. The individual source foil temperature was monitored using external thermocouple attached.

The weight of each source foil was recorded before and after plating to keep track of weight loss during each experiment. It was observed that the foils sublimed uniformly across the surface during several plating runs indicating acceptable temperature uniformity across the source surface.

A 7.6cm dia x 2.5cm thick (3"dia x1") aluminum block support was mounted at an equal distance (20cm or 8") from both zinc and cadmium source for alloy plating. This block was used as cathode base after grounding electrically. Steel coupons or substrates were placed on this cathode for plating. A thermocouple was also mounted in the center to record substrate temperature.

Mild steel has been used as a material of choice for substrate in order to simulate most practical applications. Two types of substrates were used in this research. For the statistical design experiments, small coupons, 1.27 x 1.27 cm^2 (0.5"x0.5") were cut from 2mm (0.078") thick cold rolled mild

steel sheet. For the lubricity study, 0.64cm (0.25") thick x 6.35cm (2.5") dia mild steel disks were machined. All substrates were polished and precleaned before plating as proposed. Substrates were weighed before and after each plating experiment within ±0.1mg accuracy for gravimetric thickness measurements.

4.5 Trial Settings:

The graph of Fig.8 shows the source temperature as a function of heater temperature. Also, the approximate vaporization zones are indicated according to visual observations of deposits on steel coupons. The low factorial settings (-,-) corresponding to approx. minimum acceptable deposition rate were observed to be approximately 300 °C for zinc and 230 °C for cadmium. Also, above 270 °C cadmium and 350 °C zinc source temperatures, the rates were too high for reasonable plating rate control. Accordingly, the high factor settings (+,+) for zinc and cadmium were selected somewhat lower, at 350 °C and 260 °C respectively. These observations correlated well with those published in the literature[14].

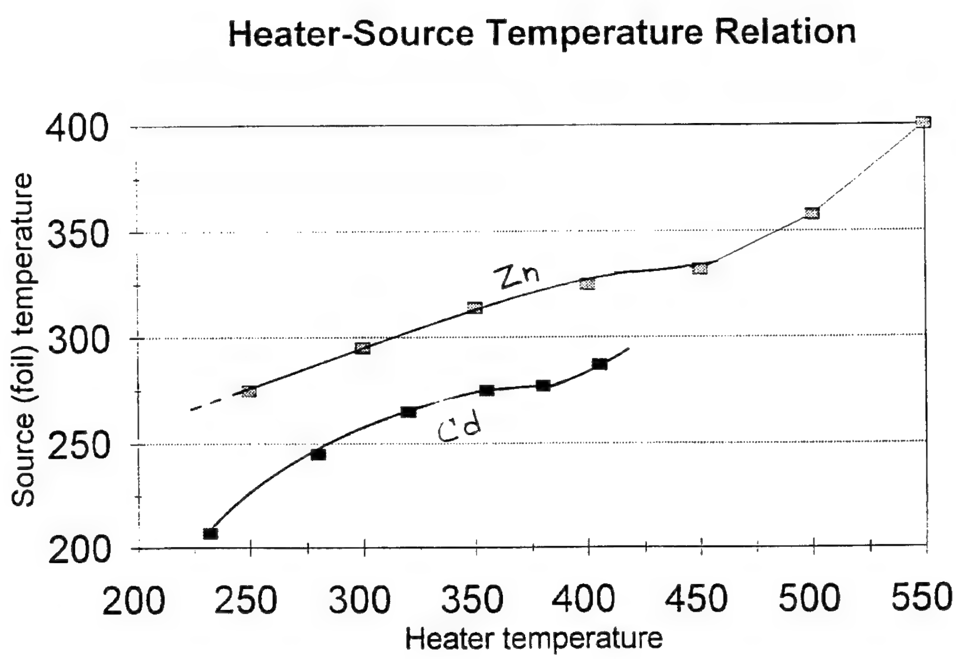


Fig.8: Heater temperature vs. source foil temperature relation.

Based on experience with the small lab apparatus, the anode bias voltage and zinc source temperature were proposed independent factors, and cadmium temperature and argon pressure were set as constants. In the new system, the relative effect of these parameters on plating was not known. Consequently, a series of preliminary alloy plating studies were conducted, with and without plasma. The major influential independent process parameters were now determined to be zinc and cadmium source temperatures. The anode bias voltage variation proposed was not effective because of the plasma distribution across the chamber influenced both source temperatures. Consequently, cadmium temperature could not be maintained constant. The new constants selected, therefore, were anode voltage and argon pressure. The trial settings and their order used for this research is shown in Table IV.

Table IV: The Trial Settings

Factor	Range	High Level	Low Level	Center Point
x_1, Cd temp	230-260 °C	260 °C	230 °C	245 °C
x_2, Zn temp	300-340 °C	340 °C	300 °C	320 °C
Factor Coding	(-) (+)	(+)	(-)	(0)

Trial Order	x_1	x_2
1	-	-
2	+	-
3	-	+
4	+	+
5	0	0

Constants: Argon pressure = 50 mT; Zinc anode bias = 380 V, 100 mA

4.6 Statistical Experiments:

A minimum of nine run factorial was required to assure that the experimental effect was at least as large as that of the experimental error. Therefore, two replicates of each trial and three replicates of the center point resulting in total 11 runs were conducted.

In order to minimize system error, the 8 runs of the design points were randomly ordered. In the test order, trials 1 to 4 were randomized first for 8 runs, and then the three center points were deliberately placed at run numbers 3, 6, and 9 to spread them through the design. Table V shows the order in which the 11 runs of the experiment were conducted and their trial settings.

Table V: Randomized test order design

Test #	Trial #	Coded		Actual Value	
		x_1	x_2	x_1	x_2
1	1	-	-	230	300
2	2	+	-	260	300
3	5	0	0	245	320
4	3	-	+	230	340
5	3	-	+	230	340
6	5	0	0	245	320
7	1	-	-	230	300
8	4	+	+	260	340
9	5	0	0	245	320
10	2	+	-	260	300
11	4	+	+	260	340

The experiments were conducted as follows. In the case of statistical modeling, two 1.27 cm^2 steel coupons were placed on the cathode base in each experiment as proposed. For lubricity study, one steel disk was plated in each experiment. The system was pumped down below $2x1^{-6}$ Torr and purged with argon for five minutes. The pressure was set to 50 mTorr (mT) and plasma parameters on the zinc side anode were set to 380 volts, 100 mA. Each source temperature was ramped up at 30 ^{o}C/min to the desired trial setting and the plating was conducted for five minutes. Only the anode on zinc side being biased, zinc vaporization was enhanced by ion bombardment. At the end of five minutes, plating was terminated and the chamber was backfilled with nitrogen. All dry plated samples were analyzed for zinc and cadmium composition using the EDS analysis at Electron Microscope Center, Colorado State University.

4.7 EDS x-ray Analysis:

This quantitative chemical analysis was performed in the Scanning Electron Microscope (SEM) by measuring the energy and intensity distribution of the x-ray signal generated by a focused electron beam. A Phillips 505 SEM with secondary, backscatter and windowless x-ray detector, and KeVex Super 8000 EDS spectrometer with associated Quantex software was used. During measurements, the incident electron beam was set at 15° to the normal to the substrate, and the x-ray detector detected characteristic x-rays emitted from the surface. To minimize measurement error due to sub-microscopic variations in composition of inhomogenous zinc-cadmium alloy, a 0.2x0.2 mm area was scanned and quantitative measurements were averaged. The accuracy of elemental composition analysis in EDS is within 1% for most metals. Both zinc and cadmium being heavy metals, this method is considered adequate for the proposed research.

4.8 Coefficient of Friction Measurements:

<u>Apparatus</u>: The purpose of this study is to observe a trend, if any, in the frictional values of zinc-cadmium alloys. A photograph of the apparatus used for friction and wear studies is shown in Fig.9.

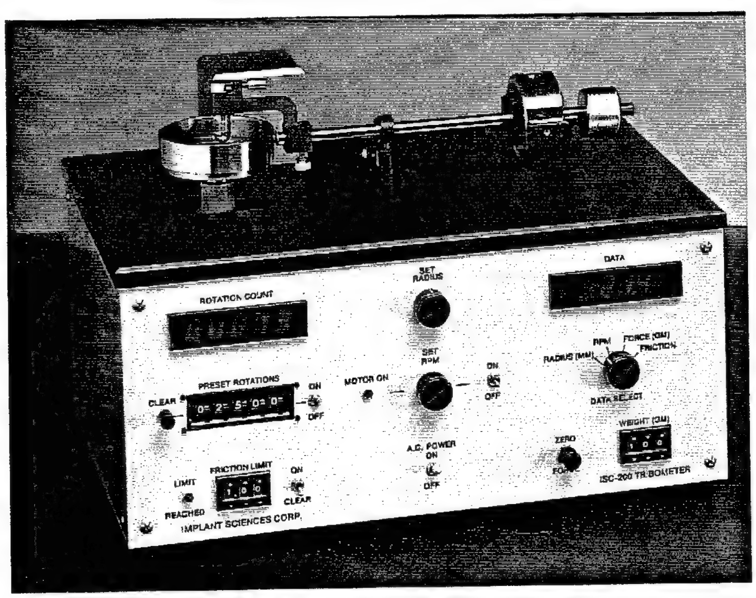


Fig.9: The pin-on-disk apparatus (Model ISC-200PC) used for lubricity study.

Frictional tests were conducted by Implant Sciences Corporation in its laboratory. In the apparatus, a lever arm is precisely balanced, and a known weight is placed on top of the attached stationary pin as normal load. Plated or coated disk in contact with the pin is turned by a motor at desired speed (typically 10 rpm to 1,000 rpm). The frictional force at the interface of pin and disk creates a drag (load). This force which is proportional to the frictional coeffefficient is translated via strain gauge to a recorder.

Measurements: A 1.27cm (0.5") dia mild steel pin tip was machined hemispherical and subsequently polished to mirror finish using 0.3 micron alumina slurry. The mild steel disks selected for the lubricity test were 6.35cm (2.5") dia. and 0.635cm (0.25") thick. These were ground to an acceptable flatness and polish on a 1500 grit SiC sandpaper. Five dry plated washers were sent to Implant Sciences of Wakefield, MA, for measurements according to specifications ASTM G-40 and G-99. Frictional tests were run without using a lubricant to simulate typical situation for cadmium plated fasteners. Fig.10 shows a photograph of the pin and a few coated sample steel substrates.

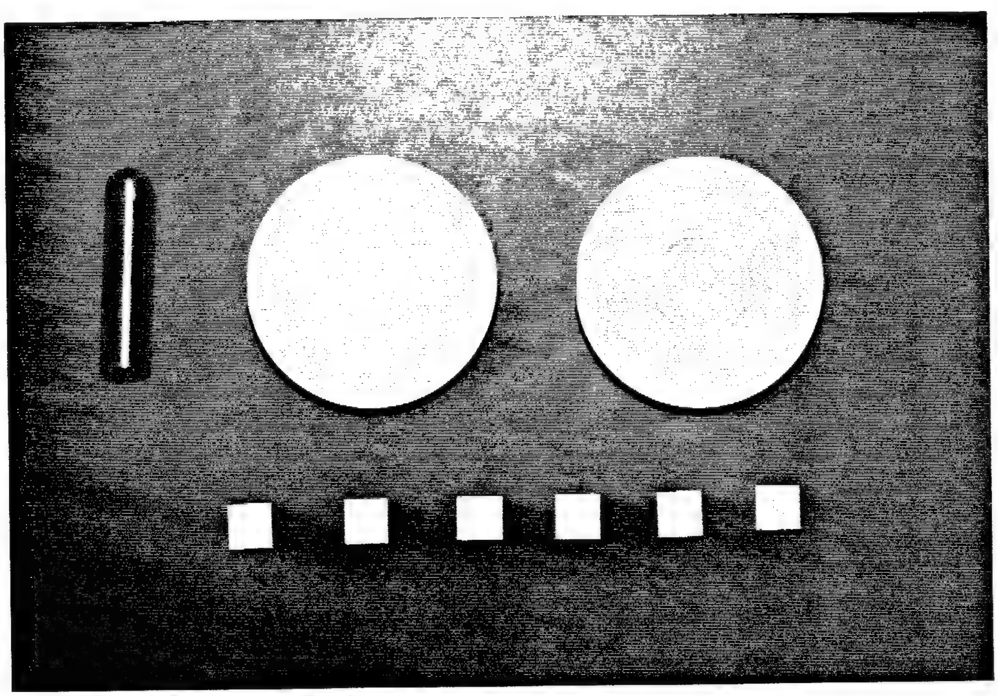


Fig.10: Tribometer pin, dry plated steel disks and coupons.

5. Results and Discussion of the Research Performed

5.1 Task I - Process Model for the Alloy Composition:

This is the primary objective of the proposed research. The modeling experiments were conducted on smaller size, 1.27x1.27 cm^2, mild steel substrates because two coupons could be placed on cathode base in each experiment. This helped to increase the sample size. The EDS analysis of the samples produced a series of plots indicating that a wide variation in the zinc content of the alloy was feasible. Two sample plots representing 12% and 56% zinc content are presented in Fig.11 and Fig.12. The experimental results of all the 11 runs are summarized in Table VI. Two observations corresponding to two replicates of each trial are entered. The percentages have been rounded off to the nearest number. The pooled standard deviation of all the observations is also noted for computational analysis.

Table VI: Summery of experimental data - % Zn in the alloy

Trial	**Code**		**y Observations, % Zn**				**Avg.**	**Variance**
#	x_1	x_2	1	2	3	4	% Zn	
1	-	-	-	56	-	56	56	0
2	+	-	9	6	12	6	8.25	8.25
3	-	+	100	100	61	96	89.25	358.25
4	+	+	98	97	80	88	90.75	71.60
5	0	0	56, 56; 56, 50; 56, 56				55.00	6.00

Note: Two observations of trial# 1 were discarded due to a known, significant experimental error.

$$\underline{\text{Pooled Standard Deviation}} = \frac{\sqrt{\text{Sum of variances}} = \sqrt{438}}{\sqrt{\text{Degrees of freedom}} = \sqrt{10}}$$

$$s_{pooled} = \mathbf{6.618}$$

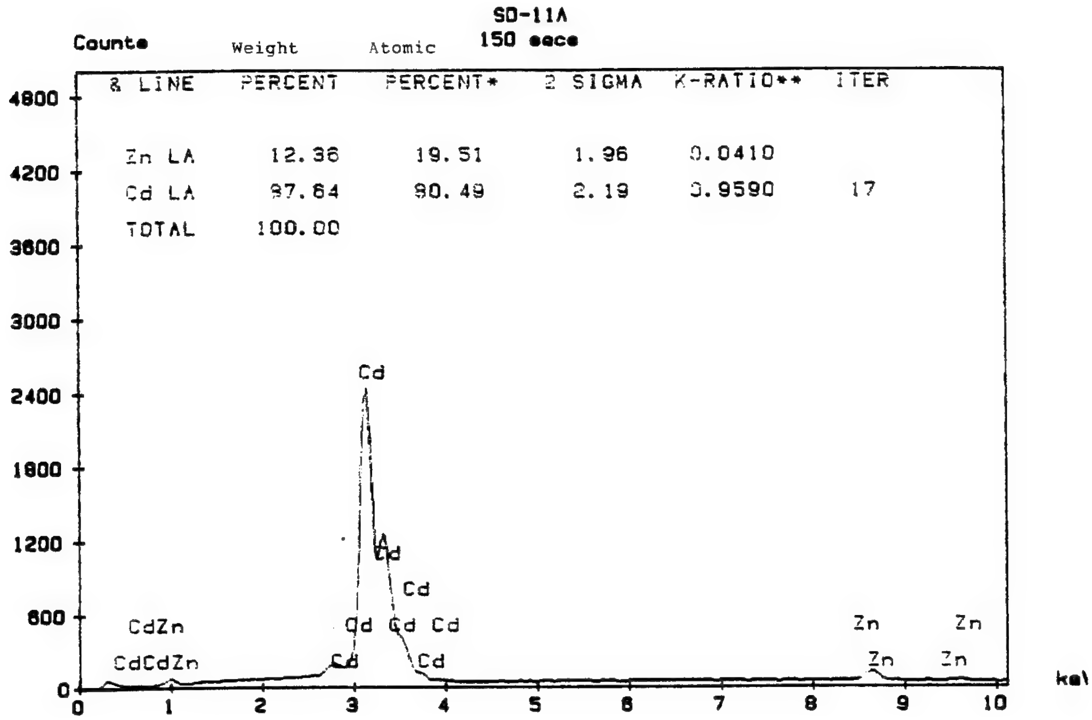


Fig.11: EDS x-ray analysis of sample SD-11A, 12% Zn in Zn-Cd.

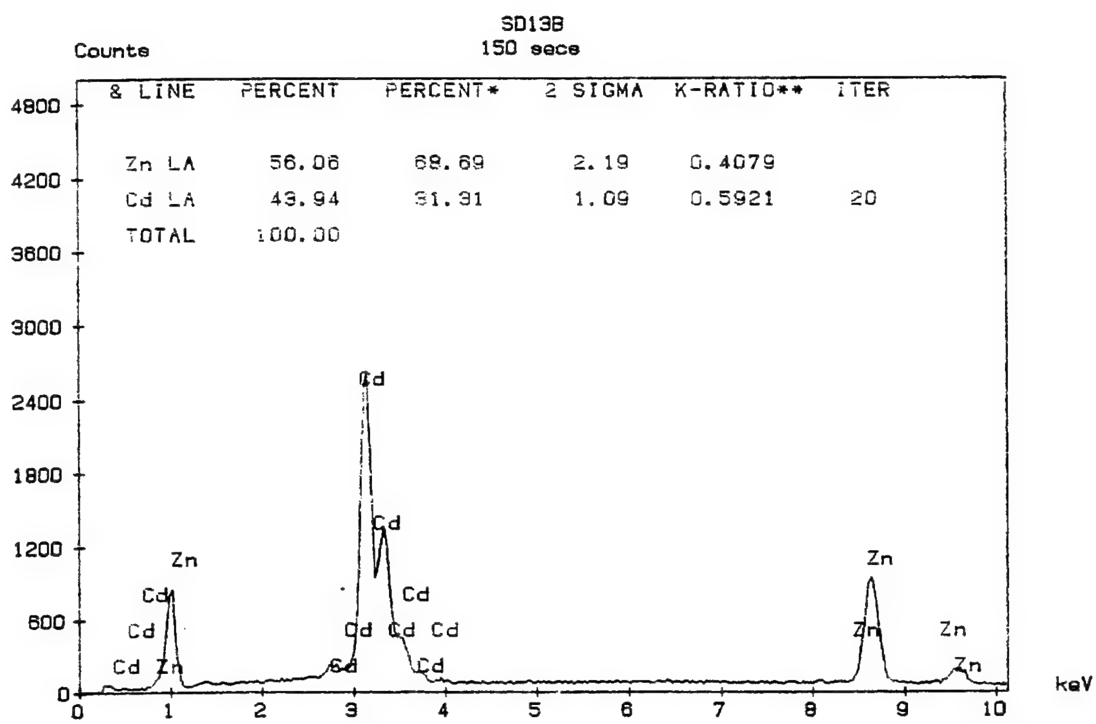


Fig.12: EDS x-ray analysis of sample SD-13B, 56%Zn in Zn-Cd.

Computational Analysis: The analysis is summarized in Table VII which gives the factor and curvature effects, and coefficients of the model.

Table VII: Factor Effect and Coefficients of the model.

Trial	Mean	x_1	x_2	x_1x_2	$y_{avg.}$
1	+	-	-	+	56.00
2	+	+	-	-	8.25
3	+	-	+	-	89.25
4	+	+	+	+	90.75
SUM(Σ) +	244.25	99.00	180.00	146.75	
SUM(Σ) -	0	145.25	64.25	97.50	
Differ.	244.25	-46.25	115.75	49.25	
Effect	61.06	-23.13	57.88	24.63	
Center Point Average = 55					
Curvature = 61.06 - 55 = 6.06					
Model					
Coeff.	**61.06**	**-11.57**	**28.94**	**12.32**	

The predicted model for the zinc composition in the alloy in this dry plating process is:

$$\textbf{\% Zn,} \quad y = 61.06 - 11.57\, x_1 + 28.94\, x_2 + 12.32\, x_1x_2$$

where x_1 and x_2 are coded factors.

Significance Check:

The minimum significance factor effect [MSF] and the minimum significant curvature [MSC] are calculated as follows:

$$MSF = ts(2/mk)^{0.5}$$

$$MSC = ts(1/mk+1/c)^{0.5}$$

For the 99% confidence level and 10 degrees of freedom in these experiments, the t value from the t-table is 3.169. Thus the minimum significant effects are

$$\mathbf{MSF} = (3.169)(6.618)[2/(2 \times 2)]^{0.5} = \mathbf{14.83}$$

and

$$\mathbf{MSC} = (3.169)(6.618)[1/(4 \times 2)+1/4]^{0.5} = \mathbf{7.302}$$

If the absolute value of a coefficient in the model equation is greater than the MSF, then the corresponding factor is considered significant. Similarly, if the value of curvature from Table VII is greater than the MSC, then the model may indicate nonlinearity in the response "y" to factor variation.

Comparing the MSF with the factor effect in the Table VII, effect of factor x_2 (Zn temp) appears relatively strong at 99% confidence level. The effect of factor x_1 (Cd temp) as well as interactive effect of x_1 and x_2 is relatively small. Comparing curvature with the MSC, the curvature effect appears significant. This means the value of zinc content is not linearly proportional to the zinc temperature. *In conclusion, it is predicted that zinc composition in the zinc-cadmium alloy is proportional to the zinc source temperature within the boundaries of the experimental space*. Consequently, the equation at 99% confidence level becomes:

$$\mathbf{y = 61.06 + 28.94\, x_2}$$

The model underlying the two-level factorial design is written in terms of coded factors x_j where

$$\mathbf{x_j} = \frac{\text{Factor level} - (\text{High} + \text{Low})/2}{(\text{High} - \text{Low})/2} \quad \text{for } j^{th} \text{ factor.}$$

For example at 330 °C zinc source temperature, the predicted zinc content of the alloy is,

$$y = 61.06 + 28.94 \times \frac{330 - (340 + 300)/2}{(340-300)/2} = 75.53\%$$

The data presented for the average values of zinc content (y Average)in the Table VII is plotted as shown in the graph of Fig.13. *The data demonstrates the feasibility of varying the proportion of zinc in the alloy plating from 8% to over 90% using the configuration proposed*. A contour map of zinc concentration using the model is shown in the Fig.14. This

map is very useful for process development work under industrial settings. For the required properties of the film, the process conditions could be selected using a contour map. Appendix B shows a full page version of this map in color.

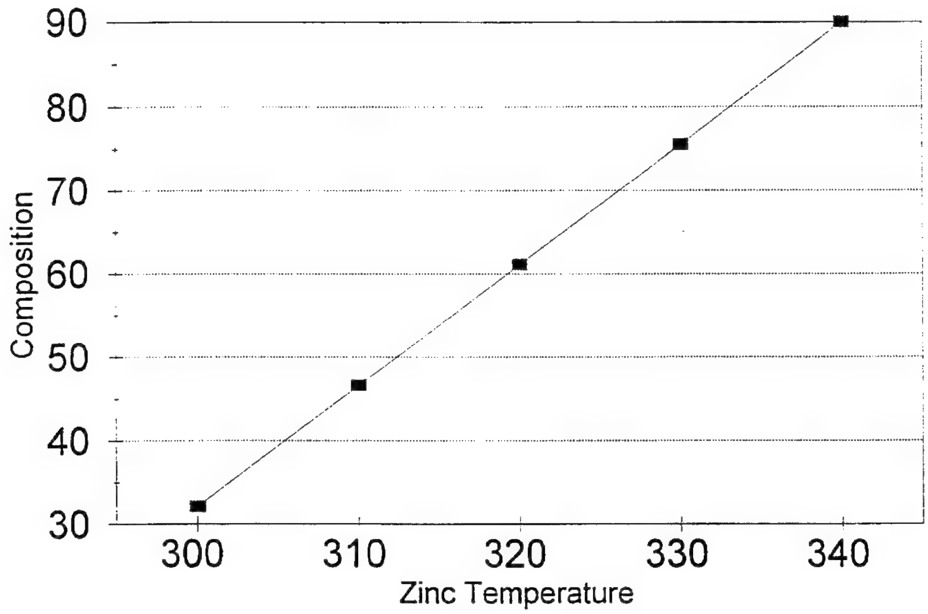


Fig.13: Zinc composition Vs. Zinc source temperature in dry plating.

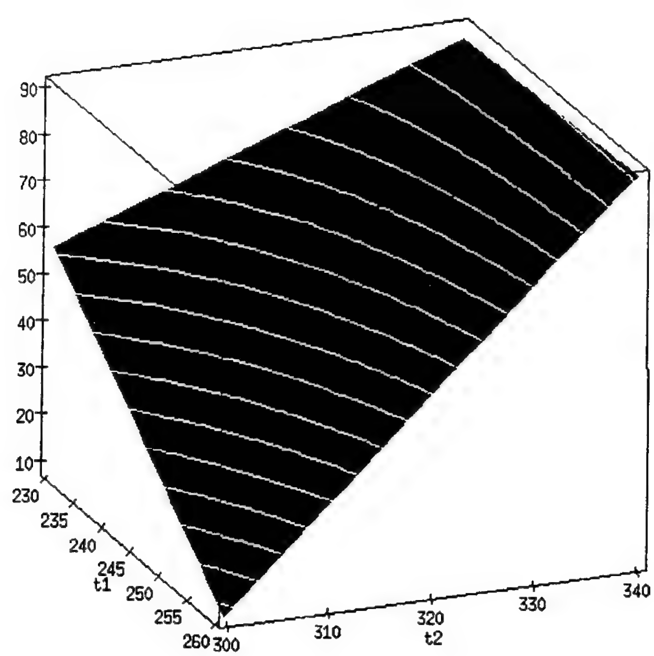


Fig.14: Contour map, zinc concentration in the alloy vs. x_1 and x_2 source temperatures.

The process model can be explained as follows. It is apparent that, in the zinc source temperature range of 300 to 340 °C, the zinc vaporization rate is relatively high compared to that of the cadmium in its range of 230 to 260 °C. In addition, the zinc vaporization was enhanced with anode bias near zinc source. This effect was noticed earlier in the preliminary studies. A marked increase in weight loss of 300 °C zinc source was observed when a 380 volt anode bias was applied, and the anode current was set at 100 mA. As a result, the effect of increase in cadmium vaporization with increased cadmium temperature may not be noticeable.

Another phenomena observed in these experiments was the accumulation of zinc deposits on cadmium source foil in dust form. The cadmium foil temperature range was not high enough to revaporize depositing zinc molecules. Consequently, this effect was minimized by using fresh cadmium foil in every run. To eliminate this concern in future systems, a higher temperature cadmium source could be used for alloy plating. In addition, direct exposure of both vaporizing foils to each other could be avoided by introducing a partition between them.

It should be emphasized here that cadmium vaporization related to factor x_1 is not entirely negligible. For example, at lower (95%) confidence level and corresponding t-static value of 2.228, both x_1 and x_1x_2 become significant. This fact strengthens the argument that the zinc vaporization is likely to be relatively strong.

A mild curvature noticed in the computational analysis is not unexpected. The vapor pressure data presented in table III is a slightly nonlinear function of temperature. In addition, the nonlinear pattern in both zinc and cadmium vaporization (Fig. ?) will be cumulative for the alloy plating. In this case, the curvature is likely to become significant. The third likely factor is the accumulation of zinc deposits on cadmium foil. However, care was taken to minimize this effect by using fresh cadmium foil in each experiment.

5.2 Task II - Frictional Measurements:

An independent evaluation and measurement of lubricity in terms for frictional coefficient was conducted by Implant Sciences Corporation. A photomicrograph in Fig. 15 shows a typical dry plated zinc-cadmium alloy surface at 300x magnification. All alloy coatings appeared dense, microcrystalline and grainy.

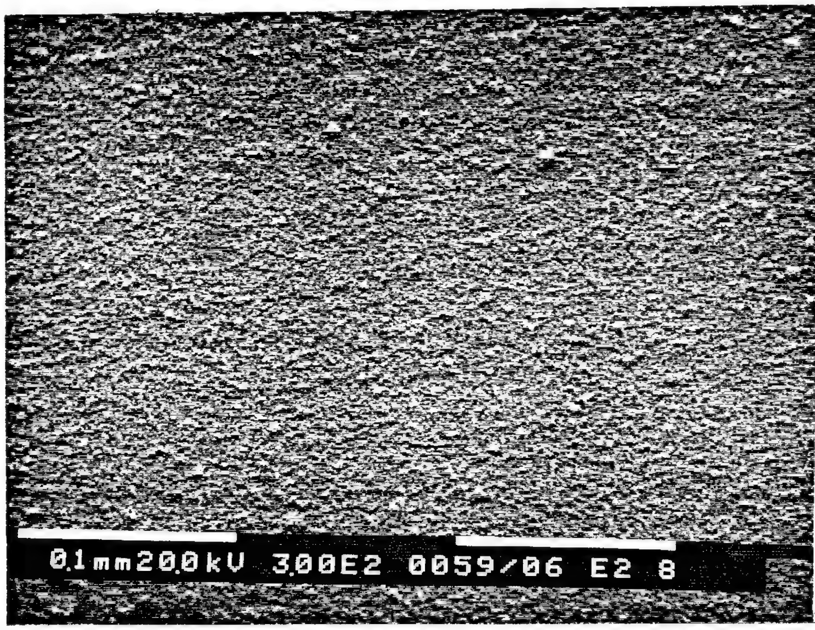


Fig. 15: Dry Plated zinc-cadmium alloy surface at 300x.

The ragged nature of the surface resulted in vibrations of the tribometer pin. This caused fluctuations in each frictional plots initially. However, due to soft nature of the materials, the wear track became smoother after about 50 to 100 revolutions. The coeff. of friction data obtained from Implant Sciences is presented in Table VIII. Also, Fig.16 shows a typical plot.

Table VIII - Coefficient of friction Data of Zn-Cd Alloys

Sample#	%Zn	%Cd	Coefff.(μ)
ZnCd-11	0	100	0.80
ZnCd-7	12	88	0.46
ZnCd-6	38	62	0.50
ZnCd-10	65	35	0.48
ZnCd-12	100	0	0.60

Note: Dry plating was conducted in random substrate order.

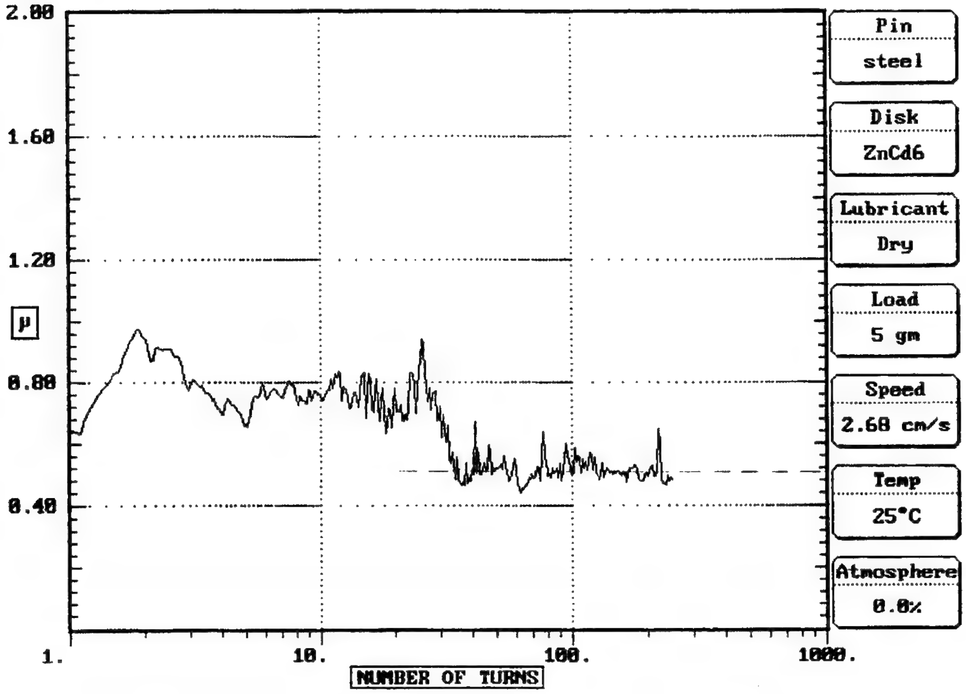
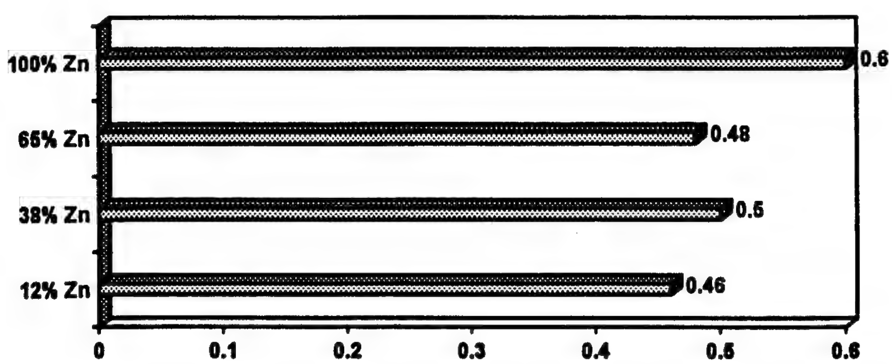


Fig.16: A typical plot after frictional coeff. measurement.

The Bar Chart of Fig. 17 shows the trend in lubricity of zinc-cadmium alloys as a function of its composition. It clearly indicates that *the coefficient of friction of zinc-cadmium alloys up to 65% zinc content is significantly lower than that of the pure zinc coating in dry plating*. This hypothesis has been confirmed using the t-static of significance at 99% confidence level as described earlier. Consequently, these alloys could be considered promising in terms of reducing the cadmium content of the coatings.



Coefficient of friction μ

Fig. 17: Trend in lubricity vs. zinc content in Zn-Cd alloys

An anomaly is also apparent in the chart. The pure cadmium coating exhibits uncharacteristically high coefficient of friction. This is analyzed as follows. In the case of hard coatings such as diamond, nitrides and carbides, weights in excess of 200 gms are typically used as normal load on the pin, and disk rotational speeds are in hundreds of rpm. However for soft surfaces like cadmium and zinc, this procedure was too severe. The metal was immediately seized, gouged and penetrated. Consequently, the following acceptable procedure was developed over a series of experiments. A 5 gm weight was placed on the pin as normal load. The disk was turned for 100 to 250 revolutions at a linear wear-track speed of ≈3cm/second or nearly 30 rpm. This procedure allowed for minimizing vibrations translated the sensitive recorder and stabilizing the measured values near 50 to 100 revolutions. However, pure cadmium was most difficult even with low load. Microscopic observations of the wear track on the disk and the tip of the pin revealed that cadmium burr accumulated on the tip within the first few revolutions. This burr started welding with the plating on the disk surface. This action is likely to result in a higher coefficient of friction. With the addition of slightly harder zinc crystals to cadmium, the alloy surface indicated improvement in measurements. The 12% zinc composition sample is likely to represent frictional coefficient nearly that of pure cadmium

Considering above observations and data, and our prior knowledge in these areas, there is considerable room for improvement in the novel zinc-cadmium alloy plating process and the new equipment hardware tested for the first time. The quality of the coating in terms of surface smoothness, density of the alloy, grain structure, corrosion resistance and other factors important to the commercial community need to be resolved. These criteria will be primarily addressed in the next phase of this project.

6. Deviations from the Proposed Research Plan

There were no deviations made in the proposed research objectives. All the objectives have been accomplished, and in the case of statistical experimental analysis, it was surpassed. As proposed, the factorial design method has been successfully applied for process modeling. Furthermore, there were four notable improvements made in the experimental plan which resulted in improving the quality of the research. These are as follows:

6.1 The New Apparatus: The apparatus proposed was a small 6" dia.x 10" tall bell-jar type available glow discharge unit with limited operating performance. On the other hand, the apparatus used has been built with wider operating range and better performance. The results obtained from this new larger system are likely to be more representative of a commercial process.

6.2 Apparatus Process Limits: These studies were not proposed in the experimental plan. The overall response of the system performance to the source heaters/temperatures, anode voltage and argon pressure was observed. A better understanding of the process was developed before beginning the factorial experiments. The process design points (factor settings) were adjusted to the limits of the experimental space as desired of a two-level factorial. An attempt has been made to account for all the experimental errors before and during the factorial so that corrective actions could be taken to minimize these errors where possible. These additional efforts have resulted in assuring the successful completion of the experimental plan. Also, the understanding of the process and the system developed during this research will likely result in successful completion of future effort.

6.3 Non-linearity Prediction: The absence of information about non-linearity in the model would have resulted in erroneous conclusion regarding the overall effect of factors on the response. The provision for curvature effect was made by adding three center points in the design and extending the experimental plan from the proposed 8 runs to 11 runs. *The process model predicted after addition of center points for source temperatures is likely to be a closer fit to the hypothetical exact model*.

6.4 Independent Lubricity Evaluation: The proposed lubricity tests were to be conducted in the Materials Laboratory at CSU. However, the resolution and accuracy of measurements of the CSU frictional tester for use on soft coatings have not been clearly defined. An independent reliable evaluation of the coating performance has been conducted at this stage of the project for more credible information.

7. Phase II Research and Development Required

In future research in dry plating related to the second phase, a prototype system needs to be developed to incorporate the three innovative approaches: the new vapor source arrangement; high vapor plating rates; and metal recycle. This prototype development activity would allow studies related to the following items:

1. optimum configuration of zinc and cadmium sources for plating,
2. optimum configuration for efficient metal reclaim and recycle,
3. process parameters required for optimum throwing power and film uniformity, cycle time, and
4. process and coating quality development studies for commercial applications.

In the dry plating unit with the metal recovery concept, one has to be careful of avoiding degradation of substrate properties. Cooling and heating mechanisms may be required for cathode and anode temperature control. In the case of environmental and safety matters, independent evaluation of the apparatus could be performed by outside laboratories and recommendations could be incorporated.

8. Future Benefits and Commercial Potential

Further development of the dry plating method will result in the following commercial benefits:

1. Simple plating operation.
2. Reclaim/recycle pure solid metal.
3. Minimize toxic waste; eliminate hazardous liquids.
4. Eliminate waste-water treatment and sludge disposal.
5. Eliminate cost of liquid chemicals related equipment.
6. Increase productivity compared to conventional vacuum plating.

The dry plating process has commercial potential in plating fasteners, electrical connectors, steel rolls and construction wire products. The distinct advantages of the dry plating process have generated substantial interest in the private sector and many federal agencies. The dry plating method has direct applications in many DoD facilities in which zinc and cadmium electroplating is currently performed. Due to the absence of hydrogen in dry plating, economical elimination of hydrogen embrittlement in critical defense systems is now feasible. In addition, available information indicates that among the high strength steel users, the U.S. Navy and Air Force are leading effort in seeking alternatives to electroplating.

The following commitments and future support has been obtained:

- The Naval Air Warfare Center, Warminster, PA has indicated active support and interest in this technology. The dry plating has potential to reduce hazardous waste in several Naval electroplating operations.

- A collaboration with the Colorado State University (CSU) has resulted in its commotment to provide research and development facilities, consulting services, equipments and laboratories on campus.

- Three private sector companies, including a venture fund, have supported and are committed to participation in the Phase

III. Follow-on funding commitment contract for the Phase III has been legally formalized.

A total of over $280,000 have been expended in the last two years and additional $90,000 have been committed to this project over the next year. However, a lot still needs to be done towards actual pilot-line set up and evaluation, customer acceptance, diversification and completion of the technology transfer to the commercial sector. This will require substantial additional funding from various resources.

9. Conclusions

This research has been concluded successfully without making significant deviations in the proposed objectives or the experimental plan. A process model for the plasma assisted zinc-cadmium alloy plating has been developed. It has been demonstrated that it is feasible to vary alloy composition in dry plating as desired by varying zinc source temperature. This would be a relatively simple procedure in commercial application. Also, lubricity of a range of zinc-cadmium alloys has been shown to be superior to that of zinc. Data in addition to that proposed has been obtained and presented. Substantial improvements were made in the proposed experimental plan to predict the models more accurately and assure the success of this Phase I effort. The understanding of the dry plating process developed in this research is valuable for future efforts in the direction of potential commercial applications. Results of this research will be directly applied in the Phase II of this project.

10. Acknowledgment

IonEdge Corporation appreciates the Office of Naval Research and the U.S. Navy for the opportunity offered to conduct this research. Support provided by the Colorado State University and its staff in research and facilities is also greatly appreciated. Special thanks to Prof. W. Sampath, Director, Materials Laboratory for valuable guidance and encouragement.

Appendix A

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Appendix B

Contour map of zinc content in the Zn-Cd alloy as a function of source tempetatures x_1 and x_2.